PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

Treatment of Cellulosic Materials

ERRATUM

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THE PATENT OFFICE
2nd December 1965

to heat, ionizing radiation or other forms of radiant energy in use, hot air drying and sterilization, for example. Discoloration of cellulosic materials is a particularly vexing problem in surgical articles such as surgical dressings, sponges and wipes since it is highly desirable that such articles be white to connote cleanliness and lack of impurities, and the usual sterilization techniques employing steam, or high energy radiation from an electron beam, Roentgen ray machine or cobalt 60 almost invariably cause substantial loss of tensile strength and yellowing of the cellulose. Although the loss in tensile strength may be tolerated in many cases, in others it may be sufficient to destroy the utility of the product. Substantial discoloration, i.e. yellowing of the cellulose, is always extremely objectionable in a normally white or colorless surgical dressing.

Various methods of reducing the discoloration of cellulosic materials have been proposed. It has previously been suggested that this be accomplished by treating the cellulose as aqueous solutions although any other suitable means of application may be employed. Any total amount of calcium, nitrate and citrate ions which is sufficient to improve the stability of the cellulosic materials against discoloration may be employed. It has been found, in general, that a useful degree of improvement in the stability of cellulosic materials is obtained by treatment with a solution having approximate contents of 0.001 to 1 percent by weight of calcium and nitrate ions and 0.001 to 1 percent by weight of citrate ions. It is generally desirable, however, to employ solutions having approximate contents of at least 0.025 percent by weight of each of the stabilizing agents in order to obtain a higher degree of stabilization. The preferred concentration of each of the components in the calcium nitrate-citric acid bath is 0.04 to 0.10 percent by weight. The stabilization procedure may be carried out by immersing or otherwise contacting the cellulosic material with the aqueous treating solution until it is

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COMPLETE SPECIFICATION

Treatment of Cellulosic Materials

We, JOHNSON & JOHNSON, a corporation organised under the laws of the State of New Jersey, United States of America, of 501 George Street, New Brunswick, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the stabilization of cellulosic materials against degradation on storage or exposure to high levels of energy.

Cellulosic materials have an inherent tendency to become discolored and lose tensile strength on storage, particularly when they have been exposed to high levels of energy. This presents a serious problem with light colored cellulosic products which must be stored or used over a prolonged period of time, particularly when they must be exposed to heat, ionizing radiation or other forms of radiant energy in use, hot air drying and sterilization, for example. Discoloration of cellulosic materials is a particularly vexing problem in surgical articles such as surgical dressings, sponges and wipes since it is highly desirable that such articles be white to connote cleanliness and lack of impurities, and the usual sterilization techniques employing steam, or high energy radiation from an electron beam, Roentgen ray machine or cobalt 60 almost invariably cause substantial loss of tensile strength and yellowing of the cellulose. Although the loss in tensile strength may be tolerated in many cases, in others it may be sufficient to destroy the utility of the product. Substantial discoloration, i.e. yellowing of the cellulose, is always extremely objectionable in a normally white or colorless surgical dressing.

Various methods of reducing the discoloration of cellulosic materials have been proposed. It has previously been suggested that this be accomplished by treating the cellulose with a small amount of tartaric, citric or gluconic acid. The present invention provides improved methods for the stabilization of cellulose against discoloration and loss of tensile strength on exposure to ionizing radiation, other high energy conditions, steam sterilization and hot air drying.

The invention is based on the unexpected discovery that the treatment of cellulosic materials with calcium and nitrate ions in combination with citrate ions achieves a dramatic reduction in the tendency of cellulosic materials to discolor and lose tensile strength. The substantial increase in stability provided by the combined calcium nitrate-citric acid system used according to the invention cannot be obtained with calcium nitrate, citric acid or citrate ions alone and is greater than the effect which would be expected from the combined effects of the individual components of the combination. It is convenient to apply the stabilizing agents to cellulosic materials as aqueous solutions although any other suitable means of application may be employed. Any total amount of calcium, nitrate and citrate ions which is sufficient to improve the stability of the cellulosic materials against discoloration may be employed. It has been found, in general, that a useful degree of improvement in the stability of cellulosic materials is obtained by treatment with a solution having approximate contents of 0.001 to 1 percent by weight of calcium and nitrate ions and 0.001 to 1 percent by weight of citrate ions. It is generally desirable, however, to employ solutions having approximate contents of at least 0.025 percent by weight of each of the stabilizing agents in order to obtain a higher degree of stabilization. The preferred concentration of each of the components in the calcium nitrate-citric acid bath is 0.04 to 0.10 percent by weight. The stabilization procedure may be carried out by immersing or otherwise contacting the cellulosic material with the aqueous treating solution until it is

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thoroughly wetted, and then removing the excess treating solution by wringing or any other suitable means. The treated material is then dried in air or a vacuum by conventional procedures to remove liquid water and leave the treating agent *in situ* on the cellulosic material. It has been found that the cellulosic material normally picks up about its own weight of treating solution although it may retain as much as 1.5 to 2 times its own weight of solution depending upon the wringing technique or other method used to remove the excess solution. It is apparent, therefore, that when the treated material is dried it will normally retain about the same concentration of treating agent by weight of the cellulose as was in the treating solution by weight of the solution although in some cases the concentration on the cellulose may be as much as 1.5 to 2 times the concentration in the treating solution.

The invention will now be described in greater detail in the following specific examples which are illustrative only and are not to be construed as limiting the invention. However, the references in the Examples to the use of calcium nitrate alone or of citric acid alone are included only for comparison and are not to be regarded as relating to the invention itself.

EXAMPLE I

Bleached cotton or viscose rayon is immersed in an aqueous treating solution containing 1 percent by weight of calcium nitrate alone or successively in separate aqueous solutions containing 1 percent by weight of citric acid and 1 per-cent by weight of calcium nitrate, respectively. The cellulose is allowed to remain in contact with each treating solution for 24 hours. At the end of this time the excess treating solution is removed from the cellulose by wringing and the damp product dried in air. The treated cellulose containing residual treating agent is then conditioned at 70 at 72°F. at a relative humidity of 65 percent until equilibrium is achieved between the cellulose and the storage atmosphere. The cellulose is then sterilized by exposure to 2.5 megarads of cobalt 60 radiation. The sterilized material is then aged under accelerated conditions by storage at 140°F. for 14 days. The relative stability of the treated cellulose is then determined by comparison of the color and tensile strength of the material with unstabilized control samples and other stabilized materials.

STANDARD TEST PROCEDURES

The relative degree of discoloration of samples of cellulose is determined according to the ASTM standard test procedure designation D 1365-55 T which employs a color difference meter available from the Gardner Laboratory, Bethesda, Maryland. The primary standard for reflectance measurement is a layer of magnesium oxide prepared according to the instructions of the National Bureau of Standards. Although other color characteristics may be compared by the standard test, the chief coordinate of interest in the present case is coordinate b which indicates specimen colors from yellow to blue; minus values of b being blue, positive values, yellow and 0.0 being the value obtained for the white primary standard described above. Because of the differences between instruments and the difficulties of making a primary standard, porcelain enamel plaques are calibrated against the primary standard and used as working standards. These plaques are available from the National Bureau of Standards, Washington D.C. and the Gardner Laboratories, Bethesda, Maryland. All values used for comparison of the relative stability of cellulose samples referred to herein are expressed in plus scalar values of the b coordinate obtained by the standard test procedure which indicates the degree of yellowing of the sample.

The tensile strength of cellulosic materials is measured according to ASTM standard test procedure designation D 1445-53 T for strength of cotton fibers (flat bundle method). This test procedure is employed for cellulosic materials of both cotton and viscose rayon to obtain the bundle strength of these materials in pounds/mg. of weight of the test material.

Samples of cotton and viscose rayon treated according to the procedure of Example I above employing successive aqueous solutions containing 1 percent of citric acid and 1 percent of calcium nitrate respectively were prepared and their stability compared with unstabilized samples of cotton and viscose rayon. The previously stabilized samples and the unstabilized control samples were all sterilized according to the procedure of Example I by exposure to 2.5 megarads of cobalt 60 radiation and aged at 140°F. for 14 days. The plus b values obtained when the samples were tested on the color difference meter according to the standard test procedure are set out in Table A below. These plus b values afford a basis for comparing the degree of yellowing and, therefore, the relative degree of stabilization of the various samples. As noted above a reading of b=0.0 indicates the color of the standard white sample whereas a plus value of b indicates yellowing; the greater the plus value of b the greater the yellowing and consequently the lower the degree of stabilization against discoloration.

TABLE A

Stability of Cellulose Sterilized by Exposure to 2.5 Megrads of Cobalt 60 Radiation and Aged at 140°F. for 14 days

Treatment of Cellulose Samples	Yellowing, Expressed in plus b Value Readings of the Gardner Color Difference Meter	
	Cotton	Viscose Rayon
Control, Not Stabilized	7.8	7.9
Treated with Aqueous Solution Containing Calcium Nitrate (1 percent by Weight)	7.2	5.3
Treated with Aqueous Solutions Containing Citric Acid and Calcium Nitrate (1 percent by Weight)	6.5	5.5

It may be seen from the data in Table A above that treatment of cotton and viscose rayon with a 1 percent solution of calcium nitrate materially improved the stability of these cellulosic materials against discoloration by exposure to high energy radiation and aging at elevated temperatures. It is also apparent that improvement was obtained in the color stability of the cellulosic materials treated according to the embodiment of the invention in which the calcium nitrate treatment was employed in conjunction with a previous citric acid treatment.

The preservation of the tensile strength of cellulosic materials according to the present invention is illustrated by determining the tensile strength of treated and untreated samples of cotton and viscose rayon by the standard ASTM D 1445-53 T flat bundle strength method. Bleached cotton, and a viscose rayon having a sodium bisulfite finish were used as controls. Other samples of the cotton and viscose rayon were exposed to 2.5 megarads of cobalt 60 radiation and aged at 140°F. for 28 days as additional controls. Still other samples of the cotton and viscose rayon were stabilized according to the procedure of Example I employing aqueous solutions containing 1 percent citric acid and 1 percent calcium nitrate by weight, exposed to 2.5 megarads of cobalt 60 radiation and aged at 140°F. for 28 days. All of these samples were then tested for tensile strength according to the standard test procedure described above. The results are set out in Table B below.

TABLE B

Tensile Strength Preservation

Treatment of Cellulose Samples	Strength According to ASTM D 1445 - 53 T Flat Bundle Test Method in pounds/mg.	
	Cotton	Viscose Rayon
Control, Untreated	6.29	4.22
Control, Irradiated and Aged	3.18	2.70
Stabilized, Irradiated and Aged	4.31	2.92

The data in Table B above show that exposure to cellulosic materials to high levels of energy such as cobalt 60 radiation and aging at elevated temperatures materially reduces tensile strength and that stabilization of the cellulose according to the invention has a substantial

preservative effect on the tensile strength of irradiated and aged cellulose.

EXAMPLE II

Bleached cotton or viscose rayon is immersed in aqueous treating solutions containing various concentrations of citric acid alone and various concentrations of calcium nitrate alone as well as in aqueous solutions containing both citric acid and calcium nitrate in various concentrations. All of the samples are allowed to remain in contact with the treating solutions for 24 hours, at the end of which time the excess treating solution is removed by wringing and the damp samples are dried in air. The treated samples are then conditioned by storage at 70 to 72°F. at a relative humidity of 65 percent until equilibrium is achieved. The relative stability of each cellulose sample is then determined by comparison of its color with cotton and viscose rayon control samples according to the standard test procedure. Data obtained on a series of cellulose samples prepared according to Example II are summarized in Table C below.

TABLE C

Stability of Cellulose Sterilized by Exposure to 2.5 Megarads of Cobalt 60 Radiation and Aged at 140°F. for 28 Days

Treatment of Cellulose Samples	Concentration of Each Treating Agent in Aqueous Solution in Percent by Weight	Yellowing, Expressed in Plus b Value Readings of the Gardner Color Difference Meter	
		Viscose Rayon	Cotton
Control, Not Stabilized	—	8.1	7.4
Calcium Nitrate+Citric Acid	0.025+0.025	6.7	—
Calcium Nitrate+Citric Acid	0.05+0.05	5.3	7.1
Calcium Nitrate+Citric Acid	0.10+0.10	5.4	6.9
Calcium Nitrate+Citric Acid	0.20+0.20	5.9	7.4
Calcium Nitrate	0.10	7.1	6.8
Calcium Nitrate	0.20	6.7	7.0
Calcium Nitrate	0.40	6.6	6.7
Citric Acid	0.05	6.8	—
Citric Acid	0.10	6.7	7.6
Citric Acid	0.20	6.4	8.9
Citric Acid	0.40	6.8	8.8

The data in Table C above show that treatment of cellulose, and particularly viscose rayon, according to the preferred embodiment of the invention in which calcium nitrate and citric acid are employed in combination, provides a greater degree of stabilization than can be achieved by either calcium nitrate or citric acid when used alone and a greater degree of stabilization than would be expected from the combination based on a knowledge of the effects obtained by the individual components.

It is apparent from the foregoing data that the present invention is capable of substantially improving the stability of cellulose even when exposed to very high levels of energy such as 2.5 megarads of cobalt 60 radiation. The invention is also useful for stabilizing cellulose when exposed to lower energy levels such as those encountered in steam steriliza-

tion. It has been found, for example, that very low concentrations of calcium nitrate and citric acid incorporated in an aqueous finishing bath are capable of stabilizing viscose rayon against discoloration during and subsequent to sterilization with steam. A series of viscose rayon samples was stabilized according to the procedure of Example II and sterilized with steam at 240 to 250°F. for 30 minutes in a stainless steel container together with a sample of bisulfite finished viscose rayon and a sample of unfinished viscose rayon as controls. These samples were tested for discoloration and tensile strength according to the standard test described above. The data obtained are summarized in Table D below.

TABLE D

Stability of Viscose Rayon Sterilized by Steam at 240 to 250°F.

Treatment of Viscose Rayon Samples	Concentration of Each Treating Agent in Aqueous Solution in Percent by Weight	Yellowing, Expressed in Plus b Value Readings of the Gardner Color Difference Meter Samples Aged at 140°F for 14 Days	Strength According to ASTM D 1445 - 53 T Flat Bundle Test Method in pounds/mg. Samples Aged at 140°F. for 28 days
Control, Bisulfite Finish	—	6.9	4.2
Control, No Finish	—	8.1	—
Calcium Nitrate+ Citric Acid	0.01+0.01	6.0	4.2
Calcium Nitrate+ Citric Acid	0.005+0.005	6.3	4.8
Calcium Nitrate+ Citric Acid	0.002+0.002	6.6	5.4
Calcium Nitrate+ Citric Acid	0.001+0.001	7.2	5.1

The data in Table D above show that the stabilizing effects of the present invention are obtained at very low concentrations of the treating agents.

Cotton gauze was stabilized according to Example II employing an aqueous solution containing 0.1 percent of calcium nitrate, 0.1 percent of citric acid and 0.18 percent of a polyoxyethylene sorbitan monolaurate containing 20 moles of ethylene oxide per mole of sorbitan monolaurate (*Tween 20* available from Atlas Powder Co.; the word "Tween" is a registered Trade Mark). This material was dried in air at 250°F. for 15 minutes and sterilized with steam at 240 to 250°F. for 30 minutes. The discoloration and reflectance of these samples were determined and compared with those of unstabilized but dried and sterilized control samples according to the standard procedure. It was found the stabilized cotton gauze had a Gardner plus b value of 3.3 and a reflectance of 89.1 after drying whereas the control sample had a b value of 4.0 and a reflectance of 87.9 under the same conditions. After steam sterilization, the stabilized material had a b value of 4.5 and a reflectance of 87.8 whereas the control had a b value of 6.6 and a reflectance of 82.8. In other words the control samples were more yellow and more gray that the treated materials both after hot air drying and after subsequent steam sterilization.

The stabilizing agents of the present invention are operable under a wide variety of conditions. They may be employed to stabilize cellulose against degradation by exposure to low energy conditions such as dry heat at temperatures of the order of 250°F. or the moist heat of steam sterilization at temperatures of 240 to 260°F. for periods of 20 to 45 minutes. The present invention employing calcium nitrate in combination with citric acid provides a method which is unique in that it is capable of stabilizing cellulosic materials against degradation on exposure to high levels of energy such as ionizing radiation. The invention is capable of providing substantial stabilization of cellulose whether exposed to mild doses of low energy infrared radiation or large doses of ionizing radiation up to 5 megarads or higher. Although it is generally preferred in the calcium nitrate-citric

acid system to employ the stabilizing agents in a ratio of 1:1 by weight, large ratios of calcium nitrate to citric acid of the order of 30:1 or more may be employed. However, since excess citric acid may have deleterious effect on cellulosic materials it is preferred to employ ratios of citric acid to calcium nitrate of no more than 2:1.

The stabilization systems of the present invention have many advantages over previously available systems, particularly for surgical purposes. Inasmuch as calcium nitrate and citric acid are fully oxidized they do not react with stainless steel hospital equipment such as sterilization vessels and hypodermic syringes, which is a disadvantage of the bisulfite stabilization systems of the prior art. This is also an advantage in that the new stabilizing systems do not reduce iodine or similar medicaments or antiseptic solutions and do not bleach dyes used in such preparations.

Unless stated otherwise all percentages, concentrations and ratios recited herein are on a weight by weight basis.

WHAT WE CLAIM IS:—

1. The method of stabilizing cellulosic materials against yellowing which comprises treating said materials with a combination of treating agents including citrate ions, calcium ions, and nitrate ions, said treating agents being applied to the cellulosic materials in amounts sufficient to improve the stability of the cellulosic materials against discoloration.

2. The method of Claim 1 in which the cellulosic material is cotton.

3. The method of Claim 1 in which the cellulosic material is viscose rayon.

4. The method of stabilizing cellulosic materials against yellowing which comprises treating said materials with a combination of treating agents in aqueous solution including citrate ions, calcium ions, and nitrate ions, each in a concentration of 0.001 to 1 percent by weight of aqueous solution.

5. The method of Claim 4 in which the cellulosic material is cotton.

6. The method of Claim 4 in which the cellulosic material is viscose rayon.

7. The method of stabilizing cellulosic materials against yellowing which comprises treating said materials with a combination of treating agents in aqueous solution including citrate ions, calcium ions, and nitrate ions, each in a concentration of 0.04 to 0.1 percent by weight of aqueous solution.

8. A method of stabilizing cellulosic materials against yellowing substantially as described in any of the Examples given above, being a method in which calcium nitrate and citric acid are used.

9. Cellulosic materials whenever treated by a method according to any of the preceding claims.

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